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Reactivity of vinyl and alkynyl zirconium complexes with the di-*ansa*-[1,1′,2,2′-bis(dimethylsilanediyl) dicyclopentadienyl] ligand

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Abstract

Vinylation of the chloro–ethyl and dichloro zirconium complexes [Zr($CpSi_2Cp$)ClX] ($CpSi_2Cp$ = 1,1′,2,2′-$(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2$; X = Et, Cl) with one or two equivalents of Mg($CH{=}CH_2$)Cl gave the new zirconacyclopentane [Zr($CpSi_2Cp$){η^2-CH_2–$(CH_2)_2$–CH_2}] and (η^4-butadiene)zirconium [Zr($CpSi_2Cp$){η^4-(butadiene)}] complexes, respectively. Addition of a toluene solution of PhC≡CPh to the zirconacyclopentane compound afforded the zirconacyclopentadiene derivative [Zr($CpSi_2Cp$){η^2-(CPh=CPh–CPh=CPh)}]. Reaction of the chloro–ethyl zirconium complex with LiC≡CPh afforded the alkynyl compound [Zr($CpSi_2Cp$)Et(C≡CPh)] which reacted with CN(2,6-$Me_2C_6H_3$) to give the insertion product [Zr($CpSi_2Cp$)(C≡CPh){η^2-C(Et)=N(2,6-$Me_2C_6H_3$)}]. Reactions of the chloro–ethyl [Zr($CpSi_2Cp$)EtCl] and alkynyl-ethyl [Zr($CpSi_2Cp$)Et(C≡CPh)] complexes with the Lewis acid $B(C_6F_5)_3$ yielding various cationic species have been monitored by ^{1}H-NMR spectroscopy. The new complexes reported and their intermediates have been identified by IR and ^{1}H- and ^{13}C-NMR spectroscopy.

Keywords: Zirconium; Alkenyl; Alkynyl; Alkylzirconacycles

1. Introduction

Bridged dicyclopentadienyl Group 4 metal complexes are particularly interesting systems, used extensively as active and stereoselective catalysts for olefin polymerization processes [1]. Their activity is increased [2] when silyl-substituted rings are used, and for this reason many studies on the synthesis and reactivity of *ansa* metallocenes of Group 4 metals with one [3] or two [4] dimethylsilyl bridges have been reported in recent years. Most of the studies concerning applications in olefin polymerization have focused on alkyl derivatives without β-hydrogen-containing alkyl groups, because of their higher stability. We recently reported [5] the synthesis and structure of β-hydrogen containing alkyl dicyclopentadienyl zirconium complexes and some aspects of their reactivity.

Dicyclopentadienyl–zirconacyclopentane compounds have been prepared by reaction of different alkenes with 'Cp_2Zr(alkene)' generated in situ [6] and by alkylation of Cp_2ZrCl_2 with 1,4-dilithiobutane and $BrMg(CH_2)_4MgBr$ [7]. These reactive compounds readily undergo reductive decoupling reactions by C_β–$C_{\beta'}$ bond cleavage in the presence of phosphine ligands to give the zirconium(II) species $Cp_2Zr(CH_2{=}CH_2)L$ [7a] and react with different alkenes and alkynes to give new zirconacyclopentane, -pentene and -pentadiene complexes [6] which have been studied particularly as stereoselective reagents for many catalytic [6,8] and stoichiometric carbon–carbon bond-forming reactions [9].

Vinyl derivatives are interesting and reactive species which provide new synthetic pathways to many related compounds. Divinyl species may rearrange to form zirconacyclopent-1-enes through β-hydrogen elimination [10] and give butadiene derivatives [11,12] by C–C coupling. The structure of such butadiene compounds has been extensively explored and their behaviour as η^4-diene or σ^2-π-zirconacyclopent-2-ene species with a

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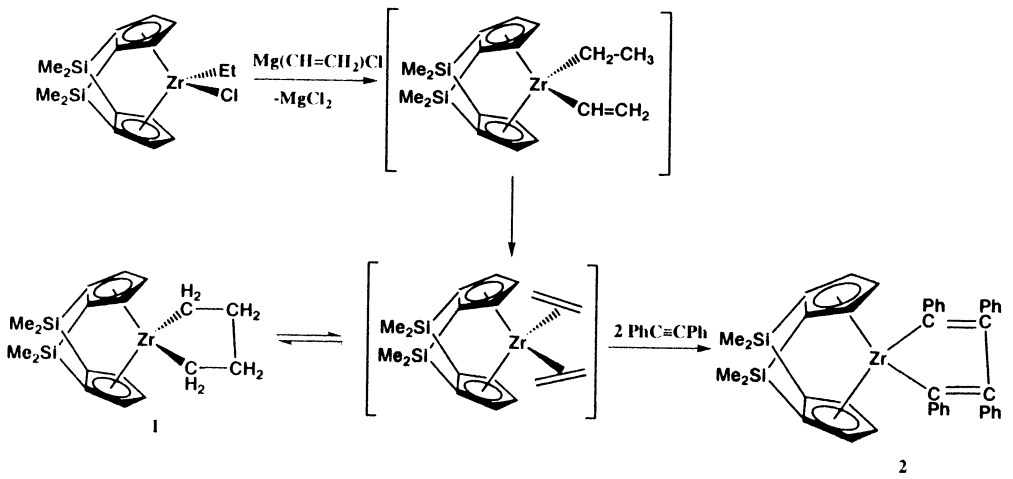


Scheme 1.

significant π-bonding contribution from the central C–C double bond has been discussed [13,14]. Because of its known higher stability, we chose the bis(dimethylsilanediyl)dicyclopentadienyl ($CpSi_2Cp$) ligand to study the behaviour of various mixed dialkyl zirconium complexes, to attempt to isolate or characterize intermediates formed during their thermal decomposition by NMR spectroscopy, and to characterize cationic species generated from their reactions with strong Lewis acids, such as $B(C_6F_5)_3$.

2. Results and discussion

2.1. Reactions with $Mg(CH{=}CH_2)Cl$

We reported [5] the isolation and thermal transformation of the β-hydrogen containing zirconium diethyl $[Zr(CpSi_2Cp)Et_2]$ derivative of the di-*ansa*-dicyclopentadienyl $[1,1',2,2'\text{-}(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]$=$[CpSi_2Cp]$ ligand. This transformation proceeds via activation of the carbon bonded β-hydrogen with elimination of ethane to give the ethylene bridged zirconium complex $[Zr(CpSi_2Cp)Et]_2(\mu\text{-}CH_2{=}CH_2)$. Hydrogen elimination from sp^2 carbon centres is less favourable and therefore the use of mixed ethyl and alkenyl compounds opens new reaction pathways. When a THF solution of the chloro–ethyl complex $[Zr(CpSi_2Cp)ClEt]$ reacted with $Mg(CH{=}CH_2)Cl$ the expected mixed alkyl–alkenyl complex was not observed even at −78°C, and the zirconacyclopentane derivative $[Zr(CpSi_2Cp)\{\eta^2\text{-}(CH_2)_4\}]$ (**1**) was immediately and quantitatively formed (see Scheme 1). Formation of **1** can be explained as resulting from a concerted ethyl β-hydrogen transfer to the α-carbon of the vinyl group located in a plane perpendicular to the equatorial metallocene plane to give the bis-ethylene complex, followed by oxidative coupling to afford the final zirconacyclopentane complex.

Complex **1** was isolated as an extremely air and moisture sensitive yellow solid. The ^{1}H-NMR spectrum of **1** showed two multiplets for the α- and β-CH_2 groups and one ABB′ spin system for two equivalent C_5H_3 rings resulting from a fast interconversion of the zirconacyclopentane. The ^{13}C-NMR spectrum showed two triplets at δ 34.8 ($^1J_{C-H} = 124.1$ Hz) and δ 23.0 ($^1J_{C-H} = 125.5$ Hz) typical for the sp^3-carbons of the zirconacyclic system and consistent with this formulation.

When the ^{1}H- and ^{13}C-NMR spectra of **1** were recorded in wet C_6D_6 the oxo-butyl complex $[Zr(CpSi_2Cp)Bu]_2(\mu\text{-}O)$, formed by hydrolytic opening of the zirconacycle, was observed[1]. However this compound could not be isolated because the reaction at a preparative level gave an unresolvable mixture of reaction products.

The di-olefin character of complex **1** (see Scheme 1) was demonstrated from its reaction in toluene with PhC≡CPh, which displaces the olefin to give the more stable zirconacyclopentadiene derivative $[Zr(CpSi_2Cp)\{\eta^2\text{-}(CPh{=}CPh{-}CPh{=}CPh)\}]$ (**2**). The formation of the zirconacyclopentene $[Zr(CpSi_2Cp)\{\eta^2\text{-}(CPh{=}CPh{-}CH_2{-}CH_2)\}]$ intermediate was observed by ^{1}H-NMR spectroscopy as a minor component in a sample of the solution taken after refluxing for 2 h. Complex **2** was isolated, after refluxing for 15 h, as a crystalline yellow solid and characterized by elemental analysis and NMR spectroscopy (see Section 4).

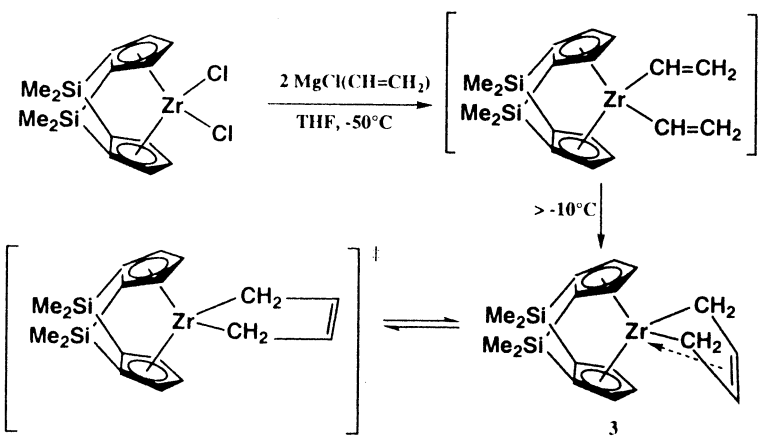
[1] NMR spectra of the major component observed when solutions of **1** were recorded in wet C_6D_6. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 6.78 (m, 4H, C_5H_3), 6.51 (m, 4H, C_5H_3), 6.09 (m, 4H, C_5H_3), 1.82, 1.16, 1.20, 0.89 (4m, 9H, Bu), 0.76 (s, 6H, $SiMe_2$), 0.60 (s, 6H, $SiMe_2$), 0.52 (s, 6H, $SiMe_2$), 0.27 (s, 6H, $SiMe_2$). ^{13}C-NMR (C_6D_6, 75 MHz, δ ppm): δ 132.0 (C_5H_3), 129.8 (C_5H_3), 120.4 (C_5H_3 C_{ipso}), 111.7 (C_5H_3 C_{ipso}), 109.8 (C_5H_3), 42.0 (Cα, Bu), 37.6 (Cβ, Bu), 30.9 (Cγ, Bu), 14.4 (Cδ, Bu), 2.7 ($SiMe_2$), 2.4 ($SiMe_2$), −2.7 ($SiMe_2$), −4.7 ($SiMe_2$).

The reaction of [Zr(CpSi$_2$Cp)Cl$_2$] [4b] with two equivalents of Mg(CH=CH$_2$)Cl in a sealed tube was monitored by ^{1}H-NMR spectroscopy in THF-d_8. No reaction was observed at −78°C but the divinyl complex [Zr(CpSi$_2$Cp)(CH=CH$_2$)$_2$}] was quantitatively formed after 5 min at −50°C, as evidenced by the ^{1}H-NMR spectrum of this solution which showed two singlets for the *exo* and *endo* silicon–methyl groups, the expected ABB′ spin system for the cyclopentadienyl ring protons, and an ABX spin system for both equivalent vinyl groups ($^3J_{trans} = 21.2$, $^3J_{cis} = 15.4$ and $^2J = 2.6$ Hz). The ^{13}C{^{1}H} spectrum showed the Cα signal at δ 184.7 (see Section 4). This divinyl complex was further transformed when the solution was heated to −10°C and after 30 min at room temperature (r.t.) gave the (η^4-butadiene) zirconium complex [Zr(CpSi$_2$Cp){η^4-(butadiene)}] (**3**) in 30% yield, together with a mixture of unidentified products. This is the transformation expected for reductive elimination [12], although the presence of other reaction products reveals that this is not a selective reaction. The r.t. ^{1}H-NMR spectrum of complex **3** shows inequivalent cyclopentadienyl rings due to a high energy barrier for the transformation shown in Scheme 2 and three multiplets for the 1,4-σ-η^2-2-butene ligand, one of them clearly shifted to high field (δ −0.80) corresponding to the butadiene H$_{anti}$ protons. This behaviour is consistent with the pronounced σ^2,π-metallacyclopentene character reported for related compounds. The high inversion barrier has been related to the stronger bonding of the butadiene internal carbon atoms for metallocenes which have narrow Cp–M–Cp angles (ca. 119°, average from six Zr(CpSi$_2$Cp) structures) [14]. This formulation is consistent with the ^{13}C-NMR spectrum, which shows six resonances for the ring carbons, two resonances for the Cα and Cβ of the butene ligand and two resonances for the silicon–methyl groups.

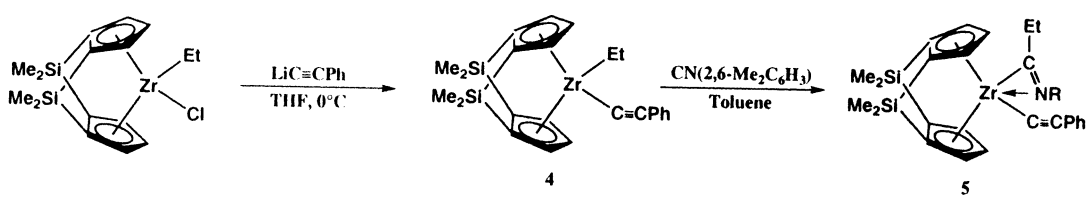
2.2. Reaction with LiC≡CPh

Reaction of the chloro–ethyl complex [Zr(CpSi$_2$Cp)EtCl] with one equivalent of LiC≡CPh in THF afforded the mixed alkyl–alkynyl complex [Zr(CpSi$_2$Cp)Et(C≡CPh)] (**4**), which was isolated as a crystalline yellow solid in 60% yield after recrystallization from pentane. β-Hydrogen elimination was not observed in a THF solution at r.t. and complex **4** was stable for short periods under these conditions. The ν(C≡C) IR absorption at 2078 cm^{-1} and characteristic resonances in its ^{1}H-NMR spectrum confirmed the presence of phenylalkynyl and ethyl ligands located in the equatorial plane, making the four silicon–methyl groups inequivalent, whereas an ABC spin system was observed for two equivalent cyclopentadienyl rings. This formulation is also consistent with the ^{13}C-NMR data (see Section 4).

Complex **4** reacted in toluene with one equivalent of CN(2,6-Me$_2$C$_6$H$_3$) which selectively inserted into the zirconium–ethyl bond to give the iminoacyl complex [Zr(CpSi$_2$Cp)(C≡CPh){η^2-C(Et)=N(2,6-Me$_2$C$_6$H$_3$}] (**5**) (Scheme 3) , isolated as a white solid in 90% yield. The IR ν(C≡C) and ν(C=N) absorptions were observed at



Scheme 2.



Scheme 3.

Table 1
^{1}H- and ^{13}C-NMR data for the ring C–H and Si–Me groups of intermediate species observed in the reactions of [Zr(CpSi$_2$Cp)EtX] (X = Cl, C≡CPh) with B(C$_6$F$_5$)$_3$ in a 1:1 molar ratio (CD$_2$Cl$_2$, 500 MHz, δ ppm)

Complex	C_5H_3	C_5H_3	Si–CH_3	Si–CH_3
[Zr(CpSi$_2$Cp)Cl(μ-Cl)	7.01 (m, 2H)	141.8, 141.0	0.99 (s, 3H); 0.97 (s, 3H)	2.0; 1.9
Zr(CpSi$_2$Cp)Et]$^+$	6.92 (m, 2H)	134.8; 132.6	0.82 (s, 3H); 0.77 (s, 3H)	1.5; 1.3
	6.61 (m, 2H)	120.8 (*ipso*); 118.1 (*ipso*)	0.76 (s, 3H); 0.42 (s, 3H)	−3.4; −3.5
	6.56 (m, 4H)	117.6; 116.6 (*ipso*)	0.40 (s, 3H); 0.26 (s, 3H)	−5.3; −5.4
	6.50 (m, 2H)	115.4; 111.5 (*ipso*)		
[Zr(CpSi$_2$Cp)Cl(μ-Cl)	7.01 (m, 4H)	135.3; 134.8	1.02 (s, 6H); 0.99 (s, 6H)	1.7; 1.6
Zr(CpSi$_2$Cp)Cl]$^+$	6.71 (m, 4H)	132.7; 116.9 (*ipso*)	0.45 (s, 6H); 0.43 (s, 6H)	−4.5; −4.6
	6.63 (m, 4H)	110.9 (*ipso*)		
[{Zr(CpSi$_2$Cp)(C≡CPh)}$_2$	6.65 (m, 4H)		0.94 (s, 6H); 0.84 (s, 6H)	
(μ-Et)]$^+$	6.57 (m, 4H)		0.77 (s, 6H); −0.14 (s, 6H)	
	5.77 (m, 4H)			

2086 and 1592 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **5** showed the expected ABC spin system for two equivalent cyclopentadienyl rings, four singlets for the silicon-bonded methyl groups and characteristic resonances for the aryl and ethyl groups. The characteristic resonance due to the η^2-iminoacyl carbon was observed in the ^{13}C{^{1}H}-NMR spectrum at δ 241.0 [15] (see Section 4).

2.3. Reactions with B(C$_6$F$_5$)$_3$

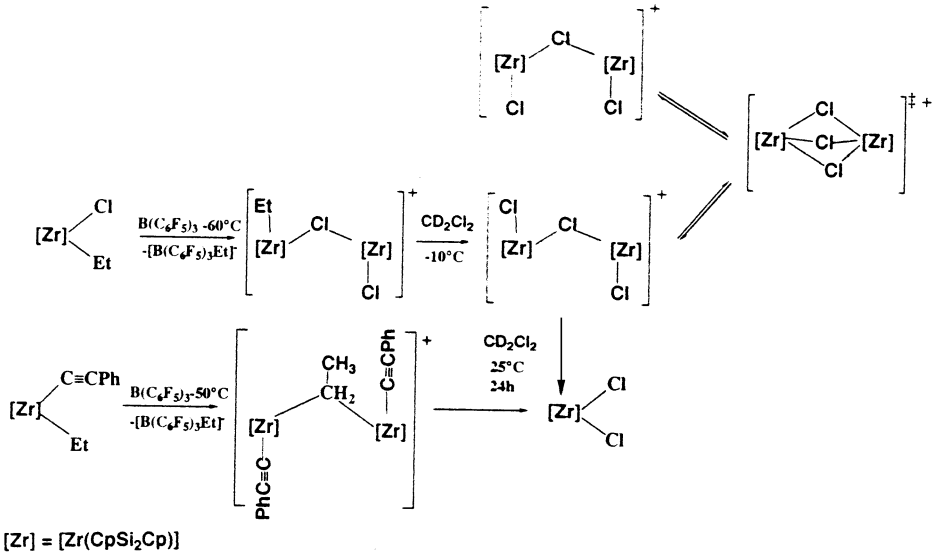
All the reactions with B(C$_6$F$_5$)$_3$, carried out in CD$_2$Cl$_2$ solutions in sealed NMR tubes and monitored by ^{1}H-NMR spectroscopy, finally gave the neutral dichloro complex [Zr(CpSi$_2$Cp)Cl$_2$] resulting from chlorination by the CD$_2$Cl$_2$ solvent. Formation of different intermediate cationic species was detected from the ^{1}H- and ^{13}C-NMR spectra recorded at different temperatures.

Addition of B(C$_6$F$_5$)$_3$ to a CD$_2$Cl$_2$ solution of the chloro–ethyl complex [Zr(CpSi$_2$Cp)ClEt] at −78°C in a 1:1 molar ratio caused the ethyl group to be eliminated to give the free anion [B(C$_6$F$_5$)$_3$Et]$^-$, as evidenced by its ^{1}H-, ^{13}C- and ^{19}F-NMR spectra [16]. The intermediate 14-electron cationic species [Zr(CpSi$_2$Cp)Cl]$^+$ initially formed was not observed and the solution remained reversibly unaltered between −70 and −10°C. As shown in Table 1 the ^{1}H- and ^{13}C-NMR spectra showed six ring-proton (two overlapping) and ten ring-carbon resonances due to two ABC spin systems for the C$_5$H$_3$ rings and eight proton and carbon resonances for the silicon-bound methyl groups. This behaviour is consistent with the presence of a dinuclear cation containing two bridged non-equivalent metal fragments, as expected for the μ-chloro bridged dinuclear species [Zr(CpSi$_2$Cp)Cl(μ-Cl)Zr(CpSi$_2$Cp)Et]$^+$, formed by coordination of one molecule of the starting chloro–ethyl complex to the initially generated chloro zirconium cation, which remained unaltered even in the presence of 1/2 equivalent excess of B(C$_6$F$_5$)$_3$. The presence of the zirconium-bound ethyl group was confirmed by the observation of an A$_2$B$_3$ spin system in the ^{1}H spectrum (δ 1.09 t, 3H, J = 7.5 Hz) and two signals at δ 16.2 and δ 61.5 in the ^{13}C-NMR spectrum.

When the temperature was raised to −10°C for 30 min the ^{1}H- and ^{13}C-NMR spectra of the resulting solution showed three proton and five carbon resonances corresponding to one ABC spin system due to four equivalent C$_5$H$_3$ rings, and four proton and carbon singlets for the silicon-bound methyl groups of a dinuclear cation which does not contain ethyl groups. This behaviour is consistent with the presence of [Zr(CpSi$_2$Cp)Cl(μ-Cl)Zr(CpSi$_2$Cp)Cl]$^+$ formed by the irreversible reaction of the previous cation with the chlorinated CD$_2$Cl$_2$ solvent [17].

This cationic species exhibited reversible dynamic behaviour between −70 and 20°C, consistent with an *anti–syn* transformation through a transition state formed by three chlorine bridges and characterized by $\Delta G^{\ddagger 263\ K} = 13$ kcal mol^{-1} at coalescence temperature (see Scheme 4). Finally a quantitative transformation led to the dichloro complex [Zr(CpSi$_2$Cp)Cl$_2$] when the solution was heated to r.t. for 24 h.

A similar study was carried out adding one equivalent of B(C$_6$F$_5$)$_3$ to one equivalent of the ethyl alkynyl complex [Zr(CpSi$_2$Cp)Et(C≡CPh)] (**4**) at −78°C in CD$_2$Cl$_2$. Formation of the [B(C$_6$F$_5$)$_3$Et]$^-$ borate anion was also observed along with a series of different cationic complexes (Scheme 4). The ^{1}H-NMR spectrum at −50°C showed one multiplet at δ −1.65 (2H) corresponding to a CH_2–CH$_3$ bridging group, an ABC spin system for four equivalent C$_5$H$_3$ rings and four singlets for the methyl–silicon protons (see Table 1). This is consistent with the presence of the cationic dimer [{Zr(CpSi$_2$Cp)(C≡CPh}$_2$(μ-CH$_2$CH$_3$)]$^+$. Between −50 and −20°C a mixture of compounds was observed, which after 1 h at −20°C contained two major components which could not be identified. A slow



Scheme 4.

transformation took place finally when the solution was heated at r.t. for more than 24 h to give the dichloro derivative [Zr(CpSi$_2$Cp)Cl$_2$].

3. Conclusions

Easy β-hydrogen elimination from the ethyl group of [Zr(CpSi$_2$Cp)EtCl] when it is vinylated is an appropriate method to synthesize the zirconacyclopentane derivative and the related zirconacyclopentadiene from its reaction with phenylacetylene. In contrast, the alkynyl compound [Zr(CpSi$_2$Cp)Et(C≡CPh)] is thermally stable and can insert isocyanide into its Zr–ethyl bond. Thermal transformation of the divinyl derivative [Zr(CpSi$_2$Cp)(CH=CH$_2$)$_2$], which can be isolated in solution between −50 and −10°C, leads to the corresponding (η^4-butadiene) zirconium complex [Zr(CpSi$_2$Cp){η^4-(butadiene)}]. Reactions of the chloro–ethyl and alkynyl–ethyl compounds with B(C$_6$F$_5$)$_3$ in sealed NMR tubes allow new dinuclear cationic species to be identified.

4. Experimental

4.1. General

All operations were performed under an inert atmosphere of argon using Schlenk and vacuum-line techniques or a VAC glovebox Model HE-63-P. The following solvents were pre-dried by standing over 4 Å molecular sieves and purified by distillation under argon before use by employing the appropriate drying/deoxygenated agents: tetrahydrofuran (sodium/benzophenone), toluene (sodium) and hexane (sodium/potassium alloy). [Zr(CpSi$_2$Cp)Cl(CH$_2$–CH$_3$)] [5], [Zr(CpSi$_2$Cp)Cl$_2$] [4b] and B(C$_6$F$_5$)$_3$ [18] were prepared according to literature procedures. Mg(CH=CH$_2$)Cl (Aldrich), PhC≡CPh (Aldrich), HC≡CPh (Aldrich), were purchased from commercial sources and used without further purification. ^{1}H- and ^{13}C-NMR spectra were recorded on Unity-300 and Unity 500 Plus spectrometers. ^{1}H and ^{13}C chemical shifts are reported in δ units measured with respect to the solvent signals. Mass spectra were recorded on a Hewlett–Packard 5890 spectrometer. Elemental C and H analyses were performed with a Perkin–Elmer 240B microanalyzer.

4.2. [Zr{(η^5-C$_5$H$_3$)$_2$[Si(CH$_3$)$_2$]$_2$}{η^2-[CH$_2$–(CH$_2$)$_2$–CH$_2$]}] (1)

A 1 M THF solution of Mg(CH=CH$_2$)Cl (2.51 ml, 2.51 mmol) was added to a toluene solution (25 ml) of [Zr(CpSi$_2$Cp)(CH$_2$–CH$_3$)Cl] (1.00 g, 2.51 mmol) at 0°C. The mixture was stirred for 2 h to give a red solution which after the solvent was removed and the residue extracted into hexane afforded complex **1**, as a yellow solid. Yield, 0.79 g, 80%. Anal. Calc. for C$_{18}$H$_{26}$Si$_2$Zr: C, 55.46; H, 6.72. Found: C, 54.92; H, 6.40%. ^{1}H-NMR (C$_6$D$_6$, 500 MHz): δ 6.64 (d, 4H, C$_5$H$_3$), 6.60 (t, 2H, C$_5$H$_3$), 1.80 (m, 4H, –CH$_2$–CH$_2$), 1.10 (m, 4H, Zr–CH$_2$), 0.47 (s, 6H, SiMe$_2$), −0.05 (s, 6H, SiMe$_2$); ^{13}C-NMR (C$_6$D$_6$, 125 MHz): δ 128.4 (C$_5$H$_3$), 114.9 (C$_5$H$_3$), 110.9 (C$_5$H$_3$ C_{ipso}), 34.8 (t, $^1J_{CH}$ = 124.1 Hz, Zr–CH$_2$–), 23.0 (t, $^1J_{CH}$ = 125.5 Hz, CH$_2$–CH$_2$), 2.0 (SiMe$_2$), −4.1 (SiMe$_2$).

4.3. [Zr{(η^5-C_5H_3)$_2$[Si(CH_3)$_2$]$_2$-{η^2(CPh=CPh–CPh=CPh)}] (**2**)

A THF solution of **1** prepared as described above from Mg(CH=CH_2)Cl (2.51 ml, 2.51 mmol) and [Zr($CpSi_2Cp$)(CH_2–CH_3)Cl] (0.99 g, 2.49 mmol) was evaporated and the residue was treated with a toluene solution (30 ml) of PhC≡CPh (0.89 g, 5.20 mmol) and then refluxed for 2 h. The ^{1}H-NMR spectrum of this solution showed that the intermediate complex [Zr($CpSi_2Cp$){η^2-(PhC=CPh–CH_2–CH_2)}] was present as a minor component. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 7.10–6.80 (m, 10H, C_6H_5 and 2H, C_5H_3), 6.72 (m, 2H, C_5H_3), 6.47 (m, 2H, C_5H_3), 2.98 (t, 2H, J_{HH} = 6.6 Hz, –CH_2–CH_2–), 1.47 (t, 2H, J_{HH} = 6.6 Hz, Zr–CH_2–), 0.52 (s, 3H, $SiMe_2$), 0.45 (s, 3H, $SiMe_2$), 0.01 (s, 3H, $SiMe_2$), −0.40 (s, 3H, $SiMe_2$). After refluxing for 15 h the solution was filtered and the solvent was removed under vacuum. The solid residue was washed with hexane (15 ml), to give a yellow solid which was characterized by NMR spectroscopy and elemental analysis as compound **2**. Yield 1.03 g, 60%. Anal. Calc. for $C_{42}H_{38}Si_2Zr$: C, 73.09; H, 5.55. Found: C, 73.42; H, 5.68%. Mass spectrum (EI): *m*/*z* 689 [M^+, 2.7], 511 [M^+ − PhC≡CPh, 2], 333 [M^+ − 2PhC≡CPh, 64.7], 178 [PhC≡CPh, 100]. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 7.10–7.04 (m, 6H, C_6H_5), 6.96 (t, 2H, C_5H_3), 6.90–6.82 (m, 8H, C_6H_5), 6.77–6.74 (m, 4H, C_6H_5), 6.80 (d, 4H, C_5H_3), 6.60–6.55 (m, 2H, C_6H_5), 0.48 (s, 6H, $SiMe_2$), −0.36 (s, 6H, $SiMe_2$); ^{13}C-NMR (C_6D_6, 75 MHz, δ ppm): δ 193.2 (Zr–CPh=), 150.7 (PhC=CPh), 141.9 (C_6H_5 C_{ipso}), 132.4, 130.2, 126.8, 124.9, 123.1 (C_6H_5), 135.5 (C_5H_3 C_{ipso}), 127.9 (C_5H_3), 116.5 (C_5H_3), 2.60 ($SiMe_2$), −5.06 ($SiMe_2$).

4.4. Reaction of [Zr{(η^5-C_5H_3)$_2$[Si(CH_3)$_2$]$_2$}Cl_2] with two equivalents of Mg(CH=CH_2)Cl

4.4.1. NMR tube scale

An NMR tube containing a mixture of the dichlorozirconocene (0.05 g, 0.12 mmol) and a 1 M THF solution of Mg(CH=CH_2)Cl (0.24 ml) in 0.75 ml of THF-d_8 was sealed under vacuum at −78°C. The reaction was monitored by ^{1}H- and ^{13}C-NMR spectroscopy. After 5 min at −50°C all of the starting complex had been transformed into [Zr($CpSi_2Cp$)-(CH=CH_2)$_2$], which was the only organometallic compound present in the solution (NMR yield, ca. 100%). ^{1}H-NMR (THF-d_8, −50°C, 500 MHz, δ ppm): δ 7.47 (dd, 2H, $^3J_{trans}$ = 21.2, $^3J_{cis}$ = 15.4 Hz, Zr–CH=), 6.43 (d, 4H, J = 2.8 Hz, C_5H_3), 6.22 (t, 2H, J = 2.8 Hz, C_5H_3), 5.87 (dd, 2H, $^3J_{cis}$ = 15.4, ^2J = 2.6 Hz, =CH_2–), 5.35 (dd, 2H, $^3J_{trans}$ = 21.2, ^2J = 2.6 Hz, =CH_2), 0.65 (s, 6H, $SiMe_2$), 0.37 (s, 6H, $SiMe_2$). ^{13}C-NMR (THF-d_8, −50°C, 125 MHz, δ ppm): δ 184.7 (–CH=), 131.5 (C_5H_3), 126.8 (=CH_2), 113.6 (C_5H_3), 110.1 (C_5H_3 C_{ipso}), 2.4 ($SiMe_2$), −4.1 ($SiMe_2$). After 30 min at 20°C, resonances of complex **3** started to appear and after 12 h at r.t. complex **3** was the major component in the solution, together with other unidentified complexes.

4.4.2. Preparative scale

A 1 M THF solution of Mg(CH=CH_2)Cl (5 ml, 5 mmol) was added to a toluene solution (50 ml) of [Zr($CpSi_2Cp$)Cl_2] (1.00 g, 2.47 mmol) at r.t. and stirred for 12 h to give a red–brown solution. The solution was filtered and the solvent was removed under vacuum to give a red oil. Recrystallization from hexane afforded the zirconacyclo-3-pentene complex [Zr(Cp-Si_2Cp){η^2-(CH_2–CH=CH–CH_2)}] (**3**) as a red solid. Yield 0.29 g, 30%. Anal. Calc. for $C_{18}H_{24}Si_2Zr$: C, 55.75; H, 6.24. Found: C, 55.54; H, 6.31%. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 6.52 (d, 2H, C_5H_3), 5.25 (d, 2H, C_5H_3), 5.05 (t, 1H, C_5H_3), 4.64 (m, 2H, –CH=), 4.14 (t, 1H, C_5H_3), 3.28 (m, 2H, –CH_2-*syn*), 0.71 (s, 6H, $SiMe_2$), 0.42 (s, 6H, $SiMe_2$), −0.80 (m, 2H, –CH_2-*anti*). ^{13}C-NMR (C_6D_6, 125 MHz, δ ppm): δ 129.8 (C_5H_3 C_{ipso}), 126.7 (C_5H_3 C_{ipso}), 124.1 (C_5H_3), 112.5 (C_5H_3), 110.7 (–CH=), 110.1 (C_5H_3), 102.4 (C_5H_3), 49.8 (dd, $^1J_{CH}$ = 158.7, $^1J_{CH}$ = 132.0 Hz, –CH_2–), 2.2 ($SiMe_2$), −3.1 ($SiMe_2$).

4.5. [Zr{(η^5-C_5H_3)$_2$[Si(CH_3)$_2$]$_2$}(C≡CPh)(CH_2–CH_3)] (**4**)

A THF (25 ml) solution of LiC≡CPh (0.11 g, 1.00 mmol) was added to a THF solution (25 ml) of [Zr($CpSi_2Cp$)Cl(CH_2CH_3)] (0.40 g, 1.00 mmol) at 0°C. The mixture was stirred for 3 h to give a dark red solution, the solvent was removed in vacuo and the residue was extracted into hexane to give complex **4**, which was recrystallized from pentane as yellow crystals. Yield 0.30 g, 64%. Anal. Calc. for $C_{24}H_{28}Si_2Zr$: C, 62.14; H, 6.08. Found: C, 61.87; H, 6.01%. IR: (Nujol) 2078 cm^{-1} [ν(C≡C)]. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 7.53 (m, 2H, C_6H_5), 7.18 (m, 2H, C_5H_3), 6.96–7.01 (m, 3H, C_6H_5), 6.51 (m, 2H, C_5H_3), 6.32 (m, 2H, C_5H_3), 1.33 (t, 3H, $^3J_{HH}$ = 8 Hz, –CH_2–CH_3), 0.72 (q, 2H, $^3J_{HH}$ = 8 Hz, –CH_2–CH_3), 0.54 (s, 3H, $SiMe_2$), 0.51 (s, 3H, $SiMe_2$), 0.50 (s, 3H, $SiMe_2$), 0.12 (s, 3H, $SiMe_2$). ^{13}C-NMR (C_6D_6, 75 MHz, δ ppm): δ 135.6 (Zr–C≡), 131.5 (C_5H_3), 129.2 (C_5H_3), 127.1 (C_6H_5), 126.0 (C_6H_5), 119.0 (≡CPh), 113.1 (C_5H_3), 111.8 (C_5H_3 C_{ipso}), 109.2 (C_5H_3 C_{ipso}), 49.5 (t, J_{CH} = 115.5 Hz, CH_2–CH_3), 13.1 (q, J_{CH} = 123.2 Hz, CH_2–CH_3), 2.42 ($SiMe_2$), 2.40 ($SiMe_2$), −3.72 ($SiMe_2$), −3.62 ($SiMe_2$).

4.6. [Zr{(η^5-C_5H_3)$_2$[Si(CH_3)$_2$]$_2$}(C≡CPh){η^2-[C(Et)N[2,6-(CH_3)$_2$$C_6H_3$]]}] (**5**)

A toluene (25 ml) solution of 2,6-dimethylphenylisocyanide (0.25 g, 1.90 mmol) was added to a toluene (25 ml) solution of [Zr($CpSi_2Cp$)Et(C≡CPh)] (**4**) (0.90 g,

1.90 mmol) at 20°C. The mixture was stirred for 12 h to give a red dark solution. Solvent was removed in vacuo and the residue extracted into hexane to yield complex **5** after evaporation. Yield 1.02 g, 90%. Anal. Calc. for $C_{33}H_{37}NSi_2Zr$: C, 66.61; H, 6.27; N, 2.35. Found: C, 66.42; H, 6.04; N, 2.34%. IR: (Nujol) 2086 [ν(C≡C)], 1592 cm^{-1} [ν(C=N)]. ^{1}H-NMR (C_6D_6, 300 MHz, δ ppm): δ 7.50 (m, 2H, C_6H_5), 7.30 (m, 2H, C_6H_5), 7.05 (t, 1H, C_6H_5), 6.94 (m, 3H, $Me_2C_6H_3$), 6.90 (m, 2H, C_5H_3), 6.59 (m, 2H, C_5H_3), 5.36 (m, 2H, C_5H_3), 2.40 (q, 2H, $J_{HH} = 7.5$ Hz, –CH_2–CH_3), 1.84 (s, 6H, $Me_2C_6H_3$), 1.11 (s, 3H, $SiMe_2$), 0.73 (t, 3H, $J_{HH} = 7.5$ Hz, –CH_2–CH_3), 0.72 (s, 3H, $SiMe_2$), 0.69 (s, 3H, $SiMe_2$), δ 0.56 (s, 3H, $SiMe_2$). ^{13}C-NMR (C_6D_6, 75 MHz, δ ppm): δ 241.0 (C=N), 145.0 (Zr–C≡), 134.8 (C_5H_3), 131.4 (Ph), 129.4 (Ph), 125.6 (Ph), 125.3 (Ph), 122.1 (C_5H_3), 118.0 (≡CPh), 109.4 (C_5H_3 C_{ipso}), 107.8 (C_5H_3), 107.3 (C_5H_3 C_{ipso}), 31.7 (t, $J_{CH} = 123.8$ Hz, CH_2–CH_3), 19.0 (q, $J_{CH} = 125.7$ Hz, $Me_2C_6H_3$), 10.1 (q, $J_{CH} = 127.5$ Hz, CH_2–CH_3), 3.2 ($SiMe_2$), 3.1 ($SiMe_2$), −3.50 ($SiMe_2$), −3.9 ($SiMe_2$).

4.7. Reaction of $[Zr\{(\eta^5\text{-}C_5H_3)_2[Si(CH_3)_2]_2\}(CH_2CH_3)Cl]$ with $B(C_6F_5)_3$

An NMR tube containing a mixture of the zirconium complex (0.05 g, 0.12 mmol) and $B(C_6F_5)_3$ (0.065 g, 0.12 mmol) in 0.75 ml of CD_2Cl_2 was sealed under vacuum at −78°C and the reaction was monitored by ^{1}H- and ^{13}C-NMR spectroscopy.

4.8. Reaction of $[Zr\{(\eta^5\text{-}C_5H_3)_2[Si(CH_3)_2]_2\}Et(C{\equiv}CPh)]$ (**4**) with $B(C_6F_5)_3$

An NMR tube containing a mixture of complex **4** (0.04 g, 0.08 mmol) and $B(C_6F_5)_3$ (0.041 g, 0.08 mmol) in 0.75 ml of CD_2Cl_2 was sealed under vacuum at −78°C. The reaction was monitored by ^{1}H-NMR spectroscopy.

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